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(54) **Fluorocarbon polymer compositions and electric cables.**

(57) A polymer composition for high-performance cables or other products requiring laser markings comprises 0.5-15% (preferably 1-10%) of a conjugated aromatic polymer (eg PEEK) dispersed in a fully fluorinated polymer matrix (eg FEP). A good white is attained without pigment, but pigments can be used eg to obtain coloured backgrounds.

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FLUOROCARBON POLYMER COMPOSITIONS AND ELECTRIC CABLES

This invention relates to fluorocarbon compositions and to products, more especially but not exclusively electric cables, in which they are used.

Polymers that are completely fluorinated, or nearly so, such as polytetrafluoro ethylene (PTFE), fluorinated ethylene-propylene copolymer (FEP) and the polymer sold under the trade mark "DuPont" as DuPont PFA are valued for high temperature rating, chemical inertness and good electrical properties; but their inert surfaces do not easily accept durable markings with inks or paints and laser printers tend to be ineffectual; in some cases the laser beam may pass through the polymer without absorption, and in others material may be ablated from the surface without any visible mark resulting; certain lasers working in the ultra-violet region do produce marks, but they are pale grey and not clearly visible.

It is an object of the present invention to provide fluorocarbon polymer compositions that accept clearly visible laser printed markings without significant detriment to temperature rating or to physical or electrical properties.

The composition in accordance with the invention comprises 0.5-15% (by weight of total polymer) of a conjugated aromatic polymer dispersed as light-scattering particles in a matrix of a substantially fully fluorinated polymer.

Preferably the content of the aromatic polymer is in the range 1-10% and more especially 1-5%; contents above 10% may lead to reduced toughness, besides being more expensive, while contents below about 1% may have less than ideal contrast. However, the precise content is not at all critical to the appearance of the markings, within the range defined.

Pigments may be present (in conventional amounts) but a good white is easily achieved without any pigments whatsoever and the use of white pigment by itself appears to have no advantages. Other minor additives can be used, if required.

Suitable conjugated aromatic polymers currently available include polyketones, polyetherketones (especially the one sold by Imperial Chemical Industries plc as PEEK), polysulphones, polyethersulphones, polyimides, polyphenylene sulphides, polyetherimides and certain liquid crystal polymers.

Infra-red, visible and ultra-violet lasers are all expected to give good results.

Examples

A series of screened 2-core aircraft cables were jacketed with the compositions shown in Table 1 below. In each case the ingredients were dried and tumble-mixed before supply to the hopper of a conventional thermoplastic-fluorocarbon extruder. The cables were marked using a YAG laser operating at 1064 nm with a beam power of about 5 W; in all cases clearly visible black markings were produced.

TABLE 1

| | | | | | | | | |
|----|--|----------|---------------|---|-----|--------------|-----|---|
| 5 | Ingredient | Example: | 1 | 2 | 3 | 4 | 5 | 6 |
| 10 | Plain clear FEP | | 9 | 9 | 9 | 9 | 9 | 9 |
| 15 | White pigmented FEP commercial masterbatch | | | | 1 | | | |
| 20 | Red pigmented FEP commercial masterbatch | | | | | 1 | 3 | |
| 25 | Plain clear PEEK | | 1 | | 0.5 | 0.5 | 1.5 | |
| 30 | White pigmented PEEK commercial masterbatch | | | 1 | | | | |
| 35 | Red pigmented PEEK commercial masterbatch | | | | | | | 1 |
| 40 | Colour | | ----White---- | | | ----Pink---- | | |
| 45 | Remarks | | A | | | | B | C |

- 50 A barely distinguishable in appearance from Examples
2 & 3, perhaps even whiter
- B darker than Example 4, but still clearly legible
- 55 C dark pink, legible but not as easily.

A series of wires were similarly coated with the compositions detailed in Tables 2 and 3. These were marked using a single pulse of radiation from a 248mm krypton fluoride excimer U.V. laser. In all cases markings clearly legible under a hand lens were obtained.

TABLE 2

| Ingredient | Example: | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|--|----------|-------------------|-----|-----|-----|-----|-----|-----|
| Plain clear FEP | | 9.7 | 9.5 | 9.3 | 9.7 | 9.5 | 9.3 | 9.5 |
| Polyether Sulphone (ICI grade 4800P) | | 0.3 | 0.5 | 0.7 | | | | |
| Polyether Ketone (ICI grade 220G) | | | | | 0.3 | 0.5 | 0.7 | |
| Polyphenylene Sulphide (Hoechst Celanese Fortran W205) | | | | | | | | 0.5 |
| Colour | | ----- White ----- | | | | | | |
| Remarks | | | | | | | | |

TABLE 3

| | | | | | | | | | |
|----|---|----------|-------------------|-----|-----|-----|-----|-----|-----|
| 5 | Ingredient | Example: | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| 10 | Plain clear FEP | | 9.9 | 9.5 | 9.7 | 9.5 | 9.7 | 9.5 | 9.3 |
| 15 | Polysulphone (Amoco P1700) | | 0.1 | 0.5 | | | | | |
| 20 | Polyetherimide (GE Plastics Ultem) | | | | 0.3 | 0.5 | | | |
| 25 | Liquid Crystal Polymer (ICI Victrex SRP) | | | | | | 0.3 | 0.5 | 0.7 |
| 30 | | | | | | | | | |
| 35 | Colour | | ----- White ----- | | | | | | |
| | | | D | | | E | | | F |
| 40 | Remarks | | | G | | | | | G |

- 45 D Slightly translucent, but still clearly legible.
- E Slightly paler mark than Example 16.
- F Slightly paler mark than Example 19.
- 50 G These samples tended to split or crack: a lower content of the aromatic polymer is recommended.

55 Claims

1. A polymer composition comprising 0.5-15% (by weight of total polymer) of a conjugated aromatic

polymer dispersed as light-scattering particles in a matrix of a substantially fully fluorinated polymer.

2 A white polymer composition in accordance with claim 1 and containing no pigment.

3. A polymer composition as claimed in claim 1 or claim 2 in which the content of the said aromatic polymer is 1-10%.

5 4. A polymer composition as claimed in claim 1 or claim 2 in which the content of the said aromatic polymer is 1-5%.

5. An electric cable with at least one component formed of the composition claimed in any one of claims 1-4.

10 6. Any article having a surface made of the composition claimed in any one of claims 1-4 and having laser-formed markings on that surface.

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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
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| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| X | EP-A-0 199 991 (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY ACADEMIA SINICA) * Claim 1; examples 7,11,12,13 * --- | 1-4 | C 08 L 27/18 H 01 B 3/44 H 01 B 7/36 |
| X | PATENT ABSTRACTS OF JAPAN, vol. 10, no. 185 (C-357)[2241], 27th June 1986; & JP-A-61 31 448 (TORAY IND. INC.) 13-02-1986 --- | 1-3 | |
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| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | C 08 L H 01 B |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 09-02-1990 | Examiner HOFFMANN K.W. |
| CATEGORY OF CITED DOCUMENTS | | | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document | |